

Improved Low Temperature Performance of Lithium Ion Cells with Quaternary Carbonate-Based Electrolytes

M. C. Smart^a, B. V. Ratnakumar^a, L. D. Whitcanack^a, K. B. Chin^a, S. Surampudi^a, H. Croft^b,
D. Tice^b and R. Staniewicz^b

^aJet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

^bSAFT America, Inc., Battery Research and Development Facility, Cockeysville, MD 20130

ABSTRACT

In order to enable future missions involving the exploration of the surface of Mars with Landers and Rovers, NASA desires long life, high energy density rechargeable batteries which can operate well at very low temperature (down to -40°C). Lithium-ion technology has been identified as being the most promising chemistry, due to high gravimetric and volumetric energy densities, as well as, long life characteristics. However, the state-of-art (SOA) technology is not sufficient to meet the needs of many applications that require excellent low temperature capabilities. To further improve this technology, work at JPL has been focused upon developing electrolytes that result in lithium-ion cells with wider temperature ranges of operation. These efforts have led to the identification of a number of ternary and quaternary, all carbonate-based electrolytes that have been demonstrated to result in improved low temperature performance in experimental three-electrode MCMB-carbon/ $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cells. A number of electrochemical characterization techniques were performed on these cells (i.e., Tafel polarization measurements, linear polarization measurements, and electrochemical impedance spectroscopy (EIS)) to further enhance our understanding of the performance limitations at low temperature. The most promising electrolyte formulations, namely 1.0 M $\text{LiPF}_6\text{EC+DEC+DMC+EMC}$ (1:1:1:2 v/v) and 1.0 M $\text{LiPF}_6\text{EC+DEC+DMC+EMC}$ (1:1:1:3 v/v), were incorporated into SAFT prototype DD-size (9 Ahr) lithium-cells for evaluation. A number of electrical tests were performed on these cells, including rate characterization as a function of temperature, cycle life characterization at different temperatures, as well as, many mission specific characterization test to determine their viability to enable future missions to Mars. Excellent performance was observed with the prototype DD-size cells over a wide temperature range (-50 to 40°C), with high specific energy being delivered at very low temperatures (i.e, over 95 Whr/Kg being delivered at -40°C using a C/10 discharge rate).

INTRODUCTION

To enable a number of future missions, NASA has interest in obtaining high specific energy rechargeable batteries which are capable of operating over a wide temperature range. To meet this need, Lithium-ion rechargeable batteries have been identified as the chemistry of choice, and have been developed for various aerospace applications under a NASA-DoD interagency program, including the Mars 2001 Surveyor Lander Program and the 2003 MER Rover program. For some of NASA's projected missions, lithium ion batteries need to be further improved, i.e., low temperature performance for Mars Landers, Rovers, and Penetrators, cycle life for the Orbiters and LEO and GEO satellites, and calendar life. Specifically, future Rover and Lander missions desire batteries which can operate at temperatures as low as -40°C . Penetrators require operation at temperatures lower than -60°C . In addition to extreme operating

temperature requirements, high specific energy (60-80 Wh/Kg) and long cycle life (< 500 cycles) are necessary for these applications. To address these issues, research is underway at JPL to improve the low temperature performance of Li-ion cells and life characteristics of Li-ion cells, with the intent of using this technology for up-coming missions. This report describes our findings on the improved performance of lithium ion cells which possess ternary and quaternary electrolytes optimized for low temperature performance consisting of mixed carbonates and having low ethylene carbonate (EC) content ($< 25\%$ EC vol%). Specifically, we have demonstrated improved low temperature with lithium ion cells containing 1.0 M $\text{LiPF}_6\text{EC+DEC+DMC+EMC}$ (1:1:1:2 v/v), 1.0 M $\text{LiPF}_6\text{EC+DEC+DMC+EMC}$ (1:1:1:3 v/v), 1.0 M $\text{LiPF}_6\text{EC+DMC+EMC}$ (15:15:70 v/v), and 1.0 M $\text{LiPF}_6\text{EC+DEC+DMC+EMC}$ (1:1:1:4 v/v). The improved performance of these electrolytes has been demonstrated in experimental three-electrode MCMB-carbon/ $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cells, as well as, in aerospace

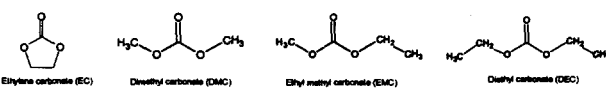
quality prototype lithium-ion cells fabricated at SAFT America, Inc.

Several factors are known to contribute to the poor low temperature performance of lithium-ion cells, including: (1) poor electrolyte conductivity, (2) poor lithium transport kinetics in the electrode materials (i.e., bulk), (3) slow diffusion and charge transfer at the electrolyte/electrode interphase, (4) poor wetting and/or transport across the separator material, (5) as well as, other cells/battery design features. Of these factors, the electrolyte type selected has the most significant impact upon the low temperature performance of Li-ion cells, due to the inherent loss in conductivity at low temperatures and the nature of the SEI layers formed on the electrodes (especially carbon), which can be highly resistive and prevent facile lithium kinetics across the electrode/electrolyte interface. For this reason, the primary focus of our work has been to develop improved low temperature electrolytes which display high conductivity and the requisite stability to ensure desirable surface films which are protective and result in long-life behavior and display good low temperature performance throughout the lifetime of the cell.

Earlier research in the area of electrolytes at JPL has resulted in the development of a system consisting of 1.0 M LiPF₆ ethylene carbonate (EC) + diethyl carbonate (DEC) + dimethyl carbonate (DMC) (1:1:1)^{1,2} which has been demonstrated to have improved performance at low temperature in prototype AA-size^{3,4}, D-size⁵, and 25 Ahr lithium-ion cells⁶, as well as, excellent ambient temperature cycle life, and acceptable storage characteristics. In addition to advances made at JPL, other groups have developed electrolyte formulations with comparable performance, including work performed by the Army Research Lab. which has resulted in 1.0 M LiPF₆ EC+DMC+EMC (1:1:1)⁷, and efforts by Covalent Associates which lead to the identification of 1.0 M LiPF₆ EC+EMC (1:3)⁸ as a good low temperature electrolyte. Although these electrolyte solutions enable efficient operation at -20°C, these formulations do not function well below -30°C. Approaches to further improving carbonate-based electrolytes include: 1) the use of low viscosity, low melting co-solvents, 2) the use of electrolyte additives aimed at improving the SEI characteristics, and 3) the use of lithium salts other than LiPF₆ and/or mixtures of electrolyte salts with the intent of either improving the low temperature conductivity or the nature of the SEI layers formed. Examples of the use of low viscosity co-solvents include the use of esters, lactones, and glymes which have been recognized to have potential for lithium batteries, including methyl formate,^{9,10,11} methyl acetate,^{12,13,14,15} ethyl acetate¹⁶, other higher molecular weight esters,^{17,18} and γ -butyrolactone,¹⁹ At JPL, we have previously reported initial results of electrolytes containing formates and esters that, in some cases, result

in improved low temperature performance, however, generally display greater reactivity than traditional carbonate-based electrolytes.^{20,21,22,23} In addition to the use of co-solvents, improvement in low temperature performance has been realized with the use of electrolyte additives, including vinylene carbonate²⁴, alkyl pyrocarbonates²⁵, and alkyl and aryl sulfites²⁶, which have been used in many cases to off-set the reactivity observed with some non-carbonate electrolyte co-solvents. Although advances have been made and highly conductive electrolyte solutions have been developed in many cases, limited success has been demonstrated to-date with systems that enables the prolonged operation of lithium ion at temperatures of -40°C and below. Given the undesirable reactivity of many of these solvents, much of our effort has involved the optimization of all carbonate-based electrolytes with the expectation of improved low temperature performance without compromising electrolyte stability.

High EC-content electrolyte formulations are desirable in terms of stability and their electrode film forming characteristics, however, the low melting point and high viscosity of EC lead to poorly conductive solutions at low temperature. Thus, it is advantageous to employ multi-component solvent mixtures to optimize cell performance over a much wider temperature range. Linear aliphatic carbonate solvents have been demonstrated to have the most utility as co-solvents in lithium-ion systems due to their low chemical and electrochemical reactivity. When assessing the relative ability of these solvents to form ionically conductive and protective surface films on the electrodes (especially on the anodes) the following trend has been observed EC > DMC > EMC > DEC. However, a reverse trend is observed for the melting points of the solvents and the viscosity. (Fig. 1)



Property	EC	DMC	EMC	DEC
MW	88.06	90.08	104.11	118.13
b.p	243	90.5	107.5	126
m.p	38	3	-14*	-43
Dielectric ϵ	89.6 (40°C)	3.12	2.96	2.82
Density (d)	1.321	1.069	1.012	0.975
Viscosity γ	1.85cP (40°C)	0.585cP	0.65cP	0.748cP
Donor #	16.4	-	-	15.1

Fig. 1. Chemical structures and properties of the cyclic and linear carbonates solvents investigated (* Value taken from 78th Edition of CRC Handbook).

Thus, to maximize the desired electrolyte properties it is beneficial to employ ternary and quaternary solvent mixtures, rather than the traditionally used binary mixtures. In this manner, electrolytes can be formulated which possess the desirable electrode filming

characteristics (imparted by EC and DMC), low melting points, and high conductivity at low temperatures (imparted by EMC and DEC). In the course of our studies, it was recognized that to achieve good performance at temperatures below -30°C , electrolyte formations consisting of mixtures of these solvents should possess less than 25% EC by volume, with the best performance being obtained with 15–20 % EC-content. In this paper, we would like to disclose recent results relating to the development of low EC-content ternary and quaternary lithium-ion electrolytes which result in good performance down to -60°C .

EXPERIMENTAL

The specific conductivities of the electrolyte solution were measured over the temperature range of -60° to 25°C using a conductivity cell, which consists of two platinized platinum electrodes immobilized in a glass apparatus and separated by a fixed distance. The cell constant of the conductivity cell was determined using a standard 0.1 M KCl solution. A Tenney environmental chamber was used to maintain the desired temperature within $\pm 1^{\circ}\text{C}$ for the cells. Samples were subjected to a minimum of two hours of soak at the desired temperature, prior to measurements. For detailed electrochemical measurements and evaluation of the electrolyte solutions, three-electrode, O-ring sealed, glass cells containing spiral rolls of MCMB carbon anode electrodes, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode electrodes, and lithium reference electrodes separated by two layers of porous polyethylene (Tonnen) were employed (~ 400 mAh capacity). The carbonate-based solvents (EC, DMC, DEC and EMC), containing LiPF_6 salt in the desired concentration, were purchased from Mitsubishi Chemicals (battery grade) with less than 50 ppm of water.

Electrochemical measurements were made using an EG&G Potentiostat/Galvanostat interfaced with an IBM PC, using Softcorr 352. A Solartron 1255 Frequency Response Analyzer was used with this potentiostat for impedance measurements, with M388 software. Charge-discharge measurements and cycling tests of the experimental cells were performed with an Arbin battery cycler. Charge-discharge measurements and cycling tests of the prototype cells (DD-Size, 9 Ahr lithium-ion cells manufactured by SAFT America, Inc.) were performed on a Maccor battery cycler.

RESULTS AND DISCUSSION

A number of ternary and quaternary ethylene carbonate (EC)-based electrolytes with varying EC-content (15–33 %) and different co-solvent mixtures have been prepared and studied, including 1.0M LiPF_6 EC+DEC+DMC+EMC (1:1:1:2 v/v), 1.0 M LiPF_6 EC+DEC+DMC+EMC (1:1:1:3), 1.0M LiPF_6 EC+DEC+DMC+EMC (1:1:1:4), and 1.0M LiPF_6 EC+

DMC+EMC (15:15:70). In addition to these low EC-content formulations, a number of other all carbonate-based electrolytes were studied as baseline solutions, including: 1.0 M LiPF_6 EC+ DMC (30:70), 1.0 M LiPF_6 EC+ DEC (30:70), 1.0M LiPF_6 EC+DEC+DMC (1:1:1), 1.0M LiPF_6 EC+DEC+DMC (4:4:2), and 1.0 M LiPF_6 EC+ EMC (1:3).

Conductivity

The specific conductivities of a number of carbonate-based electrolyte solutions were measured at different temperatures, in the range of -60°C to 25°C (Fig. 2). Of the electrolytes investigated, solutions containing a low percentage of ethylene carbonate blended with a mixture of linear carbonates displayed higher conductivity at -40°C and below. This is attributed primarily to the high viscosity and high melting point exhibited by EC when used in high proportion, resulting in poor ionic conductivity of the electrolyte. When the conductivity was measured of selected electrolytes at -40°C the following trend was observed in decreasing conductivity: 1.0 M LiPF_6 EC+DEC+DMC+EMC (1:1:1:3) (1.32 mS/cm) > 1.0 M LiPF_6 EC+DEC+DMC+EMC (1:1:1:2) (1.21 mS/cm) > 1.0M LiPF_6 EC+DEC+DMC (1:1:1) (1.01 mS/cm) > .0 M LiPF_6 EC+ DEC (30:70) (0.66 mS/cm). This trend becomes more dramatic at temperatures below -40°C when solutions containing a high proportion of EC tend to freeze and become highly viscous.

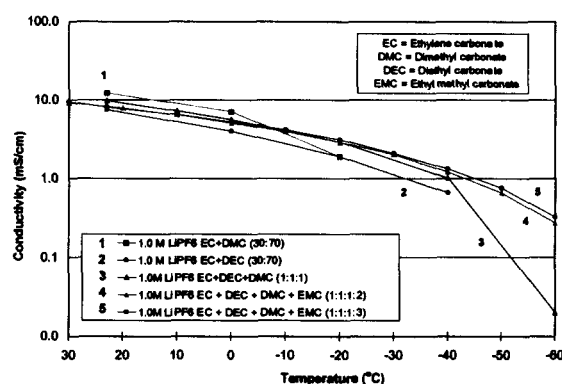


Fig. 2. Specific conductivity as a function of temperature of a number of EC-based lithium-ion electrolytes.

Charge/Discharge Characteristics

In order to effectively evaluate the potential of candidate low temperature solutions, electrolyte formulations were investigated in $\text{MCMB-LiNi}_x\text{Co}_{x-1}\text{O}_2$ experimental cells. When the cells containing the low ethylene carbonate (EC)-based electrolytes were compared with baseline formulations in terms of the reversible capacity after five formation cycles, comparable results were obtained with the cells evaluated, as shown in Fig. 3 (cell active material weights varied by less than 3%). This suggests that the low temperature electrolytes with low EC-content

possess the requisite stability and film formation characteristics to effectively passivate the electrodes and operate with the same efficacy as cells containing the baseline high EC-content electrolyte formulations.

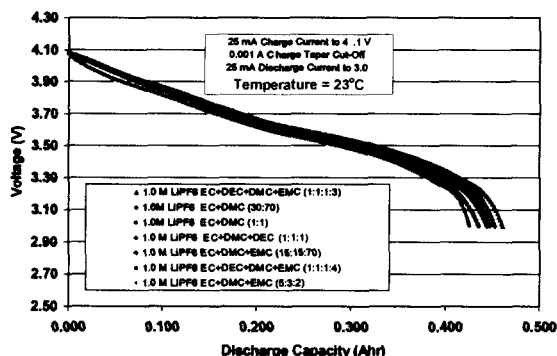


Fig. 3. Discharge capacities of MCMB-LiNiCoO₂ cells at room temperature after performing cell formation (5 cycles). Cells discharged to 3.00 V with a ~ C/15 rate (25 mA).

When the cells were discharged at -20°C (cells charged at room temperature and discharged at a ~ C/15 rate to 2.75 V), the following trend in delivered capacity was observed: 1.0M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3) > 1.0M LiPF₆ EC+ DMC+EMC (15:15:70) > 1.0M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4) > 1.0M LiPF₆ EC+DEC+DMC (1:1:1) > 1.0M LiPF₆ EC+DEC+DMC (40:40:20) > 1.0 M LiPF₆ EC+ DMC (30:70) > 1.0 M LiPF₆ EC+ DMC (50:50), as shown in Fig. 4.

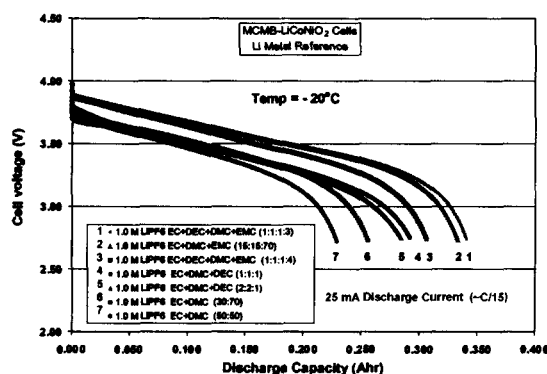


Fig. 4. Discharge capacities of MCMB-LiNiCoO₂ cells at -20°C with different carbonate- based electrolytes. Cells charged at 25°C and discharged to 2.75V using a ~ C/15 rate .

When the cells were charged at -20°C and discharged at higher rate (~ C/4 rate), the low EC-content electrolytes more dramatically outperformed the baseline electrolytes, as shown in Fig. 5. In addition to observing improvements in performance at -20°C, significant improvements in the performance at -40°C were observed with low EC-content electrolytes. As shown in Fig. 6, all of the four candidate low EC-content electrolytes performed better than the baseline solutions, delivering 50-65% of the room temperature capacity at

-40°C, with the best performance being exhibited by 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3).

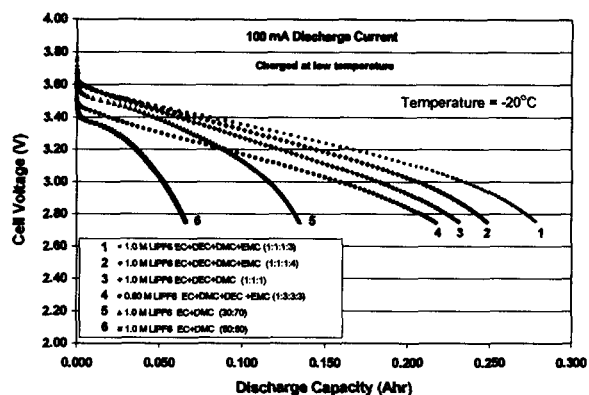


Fig. 5. Discharge capacities of MCMB-LiNiCoO₂ cells at -20°C with different carbonate- based electrolytes. Cells charged at -20°C and discharged to 2.75V at ~ C/4 rate.

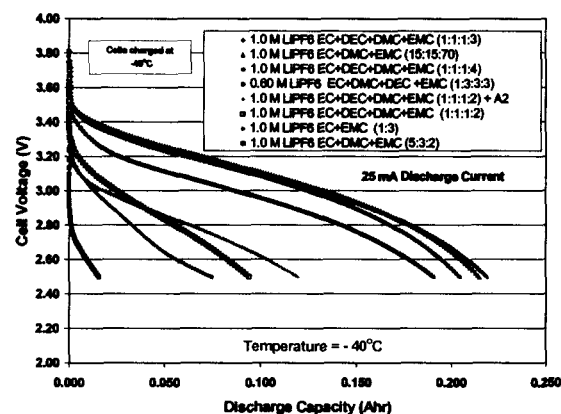


Fig. 6. Discharge capacities of MCMB-LiNiCoO₂ cells at -40°C with different carbonate- based electrolytes. Cells charged at -40°C and discharged to 2.5V using a ~ C/4 rate .

In the course of investigating these electrolytes, the use of three-electrode experimental cells was especially helpful in understanding the aspects of charging cells at low temperature, and the conditions which can lead to the phenomena of lithium plating on the anode electrode. As shown in Fig. 7, when the a cell containing a low EC-content electrolyte was cycled continuously at -20°C, the anode potential is observed to be negative with respect to the lithium reference at certain stages in the charging process (conditions of high charge current and high charge voltage). Lithium plating was not observed with the cell containing the 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3) electrolyte (observed on the subsequent discharge profile) even though the anode potential is driven negative (probably associated with the overpotential which exists for the plating reaction, the ohmic losses at low temperature, and the possibility that any plated lithium can intercalate (insert) into the carbon structure during the taper charge period). Some electrolytes, however, have resulted in systems where lithium plating occurs.²⁷ During the

course of our studies, we have observed that when the cathode kinetics are much more facile at low temperatures compared with the anode kinetics (as when the anode SEI layer is highly resistive due to undesirable decomposition of the electrolyte) lithium plating can occur with high rate charge at low temperature, the details of which will be communicated in a future publication.

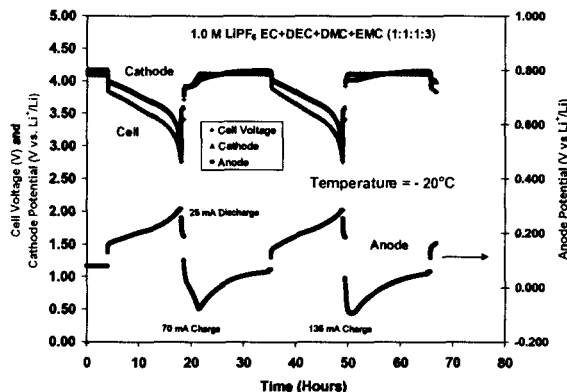


Fig. 7. Cycling characteristics of a MCMB-LiNiCoO₂ cell containing 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3) electrolyte at -20°C. Cell charged at 70 mA (~C/6) and 135 mA (~C/3) to 4.1V (with taper) and discharged at 25 mA to 2.75V.

Kinetics of Lithium Intercalation/De Intercalation

To supplement the charge-discharge data generated, we also studied the effect of different electrolytes upon the film formation characteristics on carbon electrodes (MCMB-based materials), cathode electrodes and the subsequent impact upon electrode kinetics. The nature of the SEI (solid electrolyte interphase) layers formed on the electrodes strongly influence the rate capability (intercalation and de-intercalation kinetics) of lithium ion cells, especially at low temperatures. Thus, in order to investigate these issues a number of electrochemical characterization techniques were employed including: Tafel polarization measurements, linear polarization measurements, and electrochemical impedance spectroscopy (EIS). Although all three techniques were systematically performed on the cells containing the electrolytes described, only a brief discussion will be given here and a comprehensive treatment of the kinetic measurements will be communicated in a future publication.

With the aim of getting further insight into the kinetics of lithium intercalation/de-intercalation of the carbon anodes in contrast to the mixed metal oxide cathodes in contact with these electrolytes, we have performed Tafel polarization measurements using the three-electrode experimental cells as a function of temperature. These measurements were made at scan rates slow enough (0.5 mV/s) to provide near-steady state conditions and yet with minimal changes in the state of charge of the electrode or its surface conditions. As shown in Fig. 8, when Tafel measurements were

performed on a cell containing the 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3) electrolyte at different temperatures, the limiting current densities observed on the anode were much greater than that observed with the cathode at all temperatures. This result is consistent with the fact that we did not observe lithium plating, since the cathode is preferentially polarized when attempting to charge the cell at low temperature. However, as illustrated in by the data, the differences in the electrode kinetics becomes much less dramatic at very low temperature (-40°C) suggesting that the lithium kinetics of the respective electrodes change at different rates as a function of temperature. When Tafel polarization measurements were compared for cells with different electrolyte types, it was observed that the low EC-content electrolytes displayed higher limiting current densities (on both anodes and cathodes) at low temperatures (-20 and -40°C) compared with the baseline solutions. This has been attributed to modestly higher electrolyte conductivity and favorable SEI formation characteristics of these formulations.

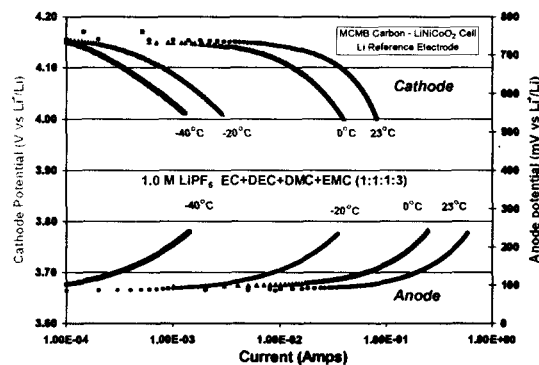


Fig. 8. Tafel polarization measurements at different temperatures performed on MCMB and LiNiCoO₂ electrodes in contact with 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3) electrolyte.

Prototype Cell Performance

In addition to evaluating these electrolytes in experimental three-electrode cells, prototype 9 Ahr lithium-ion cells (DD-size Mars Rover design) were fabricated by SAFT America, Inc. to verify the observed improved low temperature performance. As shown in Fig. 9, excellent performance was obtained with cells containing the 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3) over a wide temperature range. For example, when cells were charged at room temperature and discharged at a C/10 rate, 7.59 Ahr (95.8 WHr/Kg) was delivered at -40°C and 7.01 Ahr (78 WHr/Kg) at -50°C, corresponding to 74.6% and 68.9% of the room temperature capacity, respectively. Further improved low temperature performance was obtained with prototype DD-size cells fabricated by SAFT America, Inc. which incorporate an improved high rate anode material. When the cells were charged at room temperature and discharged at a ~ C/10 rate, 8.73 Ahr (110.0 WHr/Kg) was delivered at -40°C and 8.11 Ahr

(92.4 WHr/Kg) at -50°C , corresponding to 80.1% and 74.3% of the room temperature capacity, respectively.

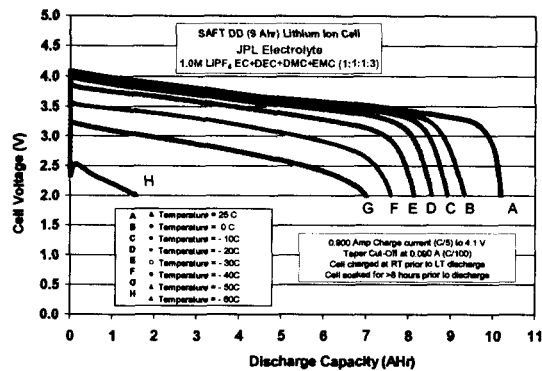


Fig. 9. Discharge capacity of a SAFT DD-size cell containing 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3) electrolyte at various temperatures (Cell charged at 25°C and discharged using a C/10 rate (0.90A) to 2.0V).

Given that many future missions require that the cells/batteries be capable of being charged at low temperatures, effort was devoted to determining the discharge rate capability at various temperatures while charging the cells at the respective temperature of interest. Good rate capability was observed at room temperature with ~ 99% of the C/10 capacity delivered at a C/2 rate. When the cells were evaluated at -20°C , good low temperature performance was realized with over 80% of the room temperature capacity being delivered at a C/2 rate. In terms of specific energy, over 133 WHr/Kg was delivered using a C/10 discharge rate and over 114 WHr/Kg was obtained using a C/2 rate (Fig. 10). This is especially significant since the charging of the cell was performed at -20°C (C/15 charge current to 4.1V).

When the cells were evaluated for their cycle life characteristics at various temperatures, as shown in Fig. 11, excellent performance was obtained even to temperatures as low as -40°C . As illustrated, when a cell was continuously cycled at -20°C using a C/10 charge rate (4.1V) and a C/5 discharge rate (to 3.0V), stable performance was obtained with over 8 Ahr being delivered, corresponding to ~80% of the room temperature capacity and over 115 WHr/Kg. Good performance was also obtained when cells were continuously cycled at -40°C . For example, when a cell was cycled at -40°C using a C/15 charge rate (to 4.1V) and a C/10 discharge rate (to 2.5 V), greater than 7 Ahr was delivered for over 95 cycles, corresponding to ~ 90 WHr/Kg and ~70% of the room temperature capacity. Under these cycling conditions, no evidence of lithium plating was observed. In addition to continuously cycling cells at -40°C using a 4.1 V charge voltage, one cell was cycled using a 4.0V charge voltage with the expectation that prolonged life will be realized due to decreased electrolyte decomposition and reduced possibility of lithium plating occurring.

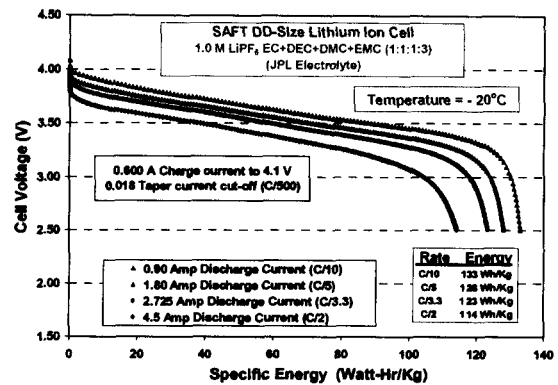


Fig. 10. Discharge rate capability of a SAFT DD-size cell containing 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3) electrolyte at -20°C , (Cell charged at low temperature).

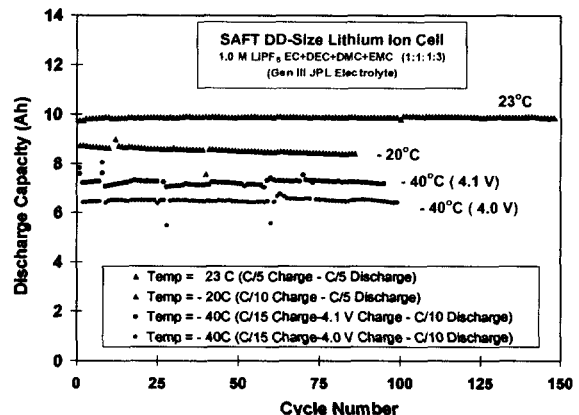


Fig. 11. Cycle life performance of SAFT DD-size cells containing 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3) electrolyte at various temperatures.

Since many of NASA's future missions would benefit from batteries which can operate at temperature below -40°C , effort was focused upon determining the performance characteristics at very low temperatures (-40° to -70°C). When cells were evaluated at -60°C , it was demonstrated that the delivered capacity increased threefold when the discharge current was reduced from a C/5 rate to a C/50 rate, corresponding to over 7 Ahr being delivered at -60°C (~ 80 WHr/Kg). It should be noted that in all cases the cell was allowed to soak at the desired temperature for 12 hours prior to discharging and thermocouples were routinely used to verify cell and chamber temperatures. Encouraged by the favorable results, we also evaluated the discharge characteristics at -70°C using low rates, as shown in Fig. 12. As illustrated, when using a C/50 discharge rate over 3.68 Ahr was delivered at -70°C , corresponding to ~ 35% of the room temperature capacity. When even lower rates are used (i.e., C/150) over 7.35 Ahr was realized, corresponding to ~ 77 WHr/Kg (or ~ 70% of the room temperature capacity). Although these rates are not sufficiently high enough to support many mission applications, they may be adequate to support a survival mode of the spacecraft vehicle during exposure to these extreme conditions.

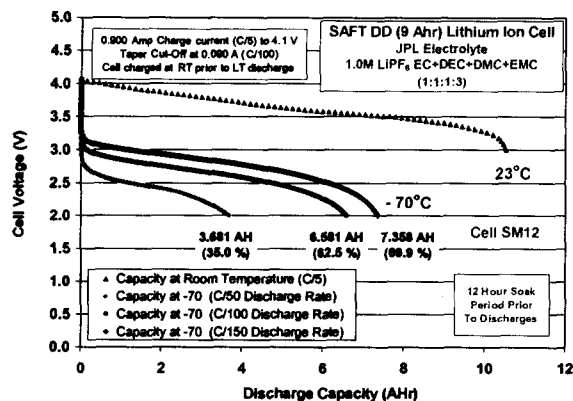


Fig. 12. Discharge rate capability of a SAFT DD-size cell containing 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3) electrolyte at -70°C, (Cell charged at room temperature).

CONCLUSIONS

A number of ternary and quaternary all carbonate-based electrolytes have been demonstrated to result in improved low temperature performance in experimental three-electrode MCMB-carbon/LiNi_{0.8}Co_{0.2}O₂ cells and prototype DD-size cells. Of the electrolytes investigated, the formulation 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3 v/v) was observed to deliver the best low temperature performance. When prototype cells containing this electrolyte were evaluated at low temperature, 8.771 Ahr (108 WHr/Kg) was delivered at -40°C with at C/10 rate and 7.555 Ahr (84 WHr/Kg) was obtained at -50°C with at C/10 rate (room temperature charge). In addition to the observed excellent discharge characteristics, cells were capable of being continuously cycled at -40°C while still delivering ~90 WHr/Kg and ~70% of the room temperature capacity. These cells were demonstrated to operate to temperatures as low as -70°C using low rate discharge (i.e., 33 WHr/kg and 77 Whr/Kg being delivered at C/50 and C/150, respectively).

Acknowledgements

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